

# **Chapter 6**

## **Quality Control of Electroless Nickel Deposits**

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Electroless nickel deposits are smooth, hard nickel-phosphorus alloy coatings produced by a chemical reduction reaction. The properties of these coatings are dependent upon the substrate, pretreatment, plating process, composition of deposits, and post treatments. This interdependency of processes and materials on the performance of the coating makes quality control and process control key aspects of the manufacturing system.

In most applications, electroless nickel is used because of aggressive corrosion or wear conditions on the base material. In these applications, the coating performance can be critical to the overall system, and the potential loss to society if the coating fails significant.

Changes in coating performance, like surface finish and porosity, are affected by the manufacturing process before plating and bath formulation, while thickness, adhesion, and hardness are dependent on the plating process. Many times a combination of effects will influence the performance of the coating.

Electroless nickel deposit properties can also vary significantly between types of solutions. This is a result of the electropotential in the application environment and differences in the coating structure.

These chemical and physical changes in the deposit can be related to the phosphorus content and the number of lattice defects in the structure. By design, some types of solutions have greater numbers of lattice defects than others. Generally, as the lattice defects in the alloy increase, the deposit becomes more brittle and harder with a reduction in the modulus and increase in tensile strength.

The control of these properties is accomplished by maintaining the plating solution within a narrow operating range and controlling trace elements such as sulfur, antimony, cadmium, and bismuth, which are generally attributed with having the greatest effect on the structure and composition of the deposit.

### **QUALITY METHOD**

Developing a method of controlling the factors that affect quality requires an overall scheme. This scheme must identify the quality level, analyze the process system to identify critical conditions, modify the manufacturing process, and

identify the new quality level. Many methods have been developed to describe the relationship of quality to manufacturing process. One that works well for metal finishing is based on the work of Taguchi (Fig. 6.1).

According to his method, the goal is to develop a more robust manufacturing system that has no performance variation of the product, while experiencing a higher level of *noise* or variations within the processes.

The term *noise* is used to describe process variations from a mean. These variations can be from the wear of machines, operator training, contamination of materials, as well as many other factors. The use of the term *inner noise* refers to variations that are being monitored and can be controlled, while *outer noise* refers to variations that are not being controlled.

In Fig. 6.1, the block "Off-line Quality Control" is generally provided by the suppliers of processes, while "Transfer Design" and "On-line Quality Control" are performed by the producing facility.

When these basic concepts are transferred to a shop floor system, several familiar shop functions are revealed. The first item is the *specification*, which describes the requirements by acceptance and qualification tests that must be completed to verify the quality of the coating. In addition to the specification, a *shop traveler* is used to transfer the designs to the processor. This document includes the sequence, conditions, times, and other critical information needed to produce a quality part. A phase of the design includes the frequency of testing of process conditions, which allows the process engineer to determine the *Process Capability Index*.

By following the shop traveler and collecting the process information, studies on the coating performance can be related to process conditions, different operators, base materials, and more. From these studies, the frequency of testing can be modified, new, more robust conditions can be selected, and the quality can be brought under control.

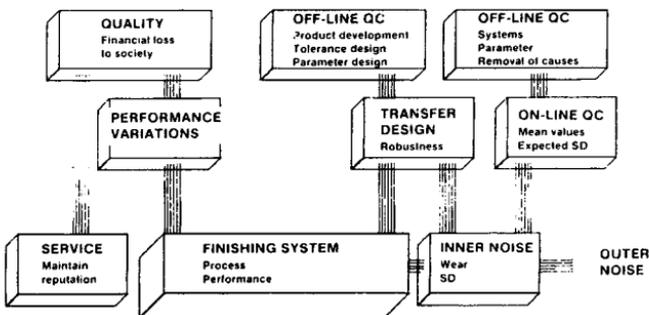


Fig. 6.1—Quality control and process management.

Experience and the pursuit of these methodologies has provided the information to build a series of cause and effect charts covering the electroless nickel process (see Charts 6.1-6.4). These charts describe the relationship of a coating failure to the processes.

Figure 6.2 shows the three areas that require control by operators: (a) process analysis and history; (b) qualification tests; and (c) acceptance tests.

### **Process Analysis and Management**

In order to maintain the quality of the electroless nickel deposit, the electroless solution must be maintained at optimum chemical and physical condition.

Constant filtration of the plating solution is recommended. The solution should be filtered more than 10 times the volume of the process every hour. At this rate of filtration, the filter will be able to remove most of the solids and prevent the formation of roughness on the parts.

An important aspect in the design of the filter system is the pump dynamics and how the system will operate with a high specific gravity and temperature. The system should be sized for an operating temperature of 195° F and a specific gravity of 1.310.

The maintenance of a relatively narrow pH range will insure a constant plating rate and phosphorus content in the alloy. A pH change of 0.1 points may cause a variation of 0.1 mil/hr and affect the final product performance and cost. For some solutions, a change in pH of 0.5 points will cause a 1 percent change in phosphorus content and significantly affect the properties of the subsequent deposit.

Maintenance of the chemical composition of the plating solution in general, and the nickel/hypophosphite ratio in particular, will ensure a uniform plating rate and phosphorus content. Air agitation and low loading will cause oxidation of the available hypophosphite and may lead to a lower phosphorus content in the deposit and slower plating rates. To overcome this, periodic titrations for sodium hypophosphite and additions in the form of replenisher should be made to the plating solution.

The concentration of trace metals within the plating solution will also affect the deposit properties. There are several elements that will directly affect the performance in all solutions. These include sulfur, iron, cadmium, bismuth, antimony, mercury, lead, and zinc. There are several others that may affect the deposit properties, and which are primarily controlled by atomic adsorption, inductively coupled plasma, or polarography. The presence of some of these materials may cause porosity in thin deposits and high stress. Some trace metals increase the propensity to pitting in the environment by setting up active cells on the surface between nickel and the trace element. Excessive concentration of trace elements in the solution may also produce a condition called *step plating*, in which edges are not plated or areas have low thicknesses.

The control of trace elements starts with keeping them out the solution. If they are present, several techniques can be tried to reduce their effect. Dilution is the first choice, followed by dummying, and addition of secondary reducing agents. Generally a combination of treatments will reduce the effect of the trace elements and bring the solution back to a productive condition.

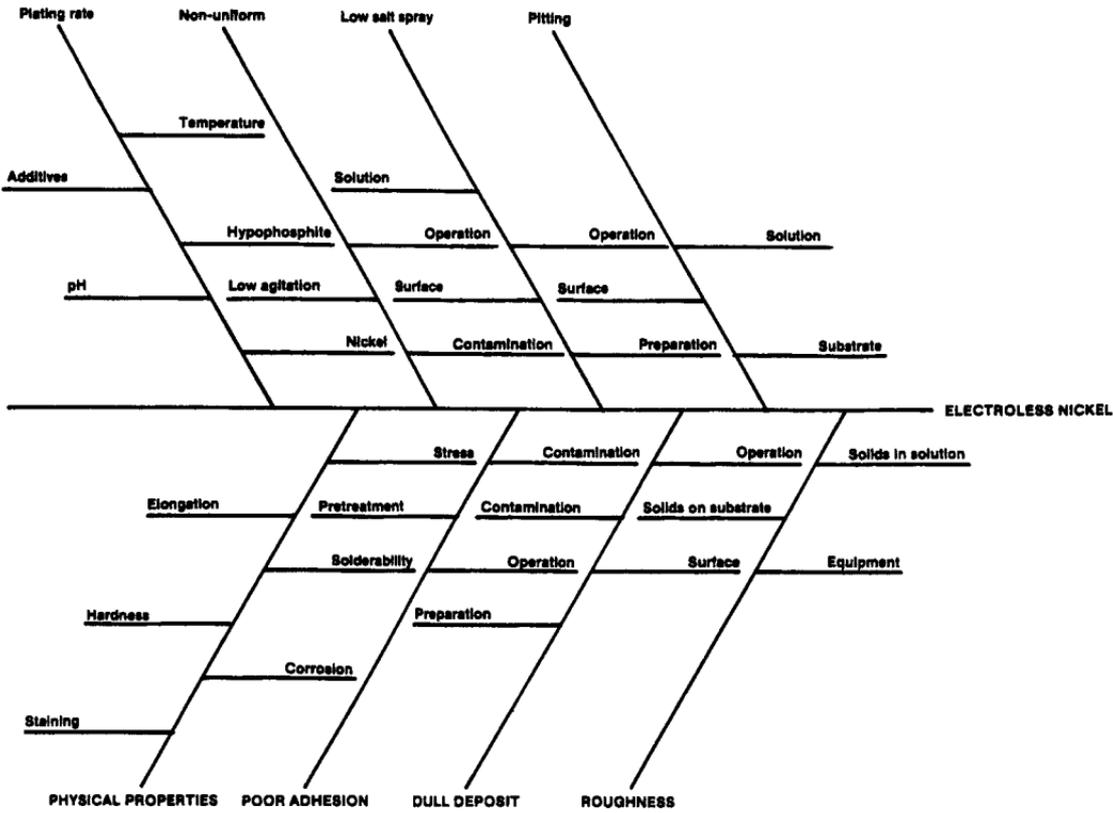


Chart 6.1—Cause-and-effect chart for electroless nickel, showing major defects and possible causes.

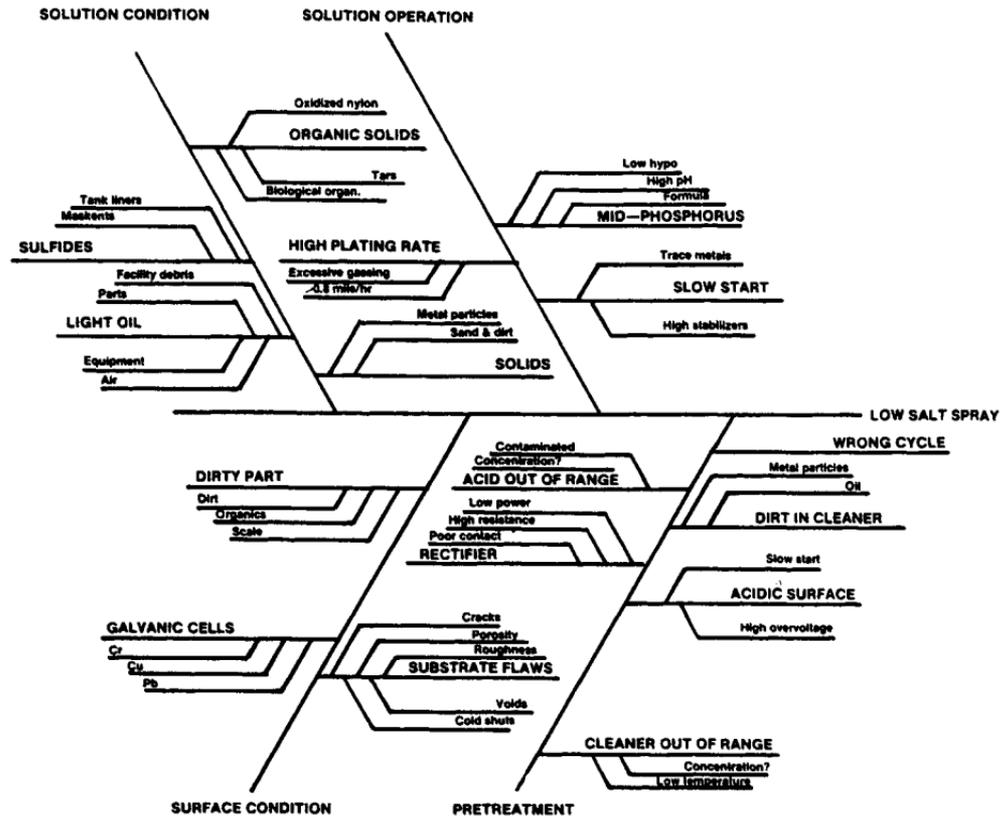


Chart 6.2—Cause-and-effect chart for the effect of electroless nickel with low salt spray resistance, showing some of the causes for such a condition.

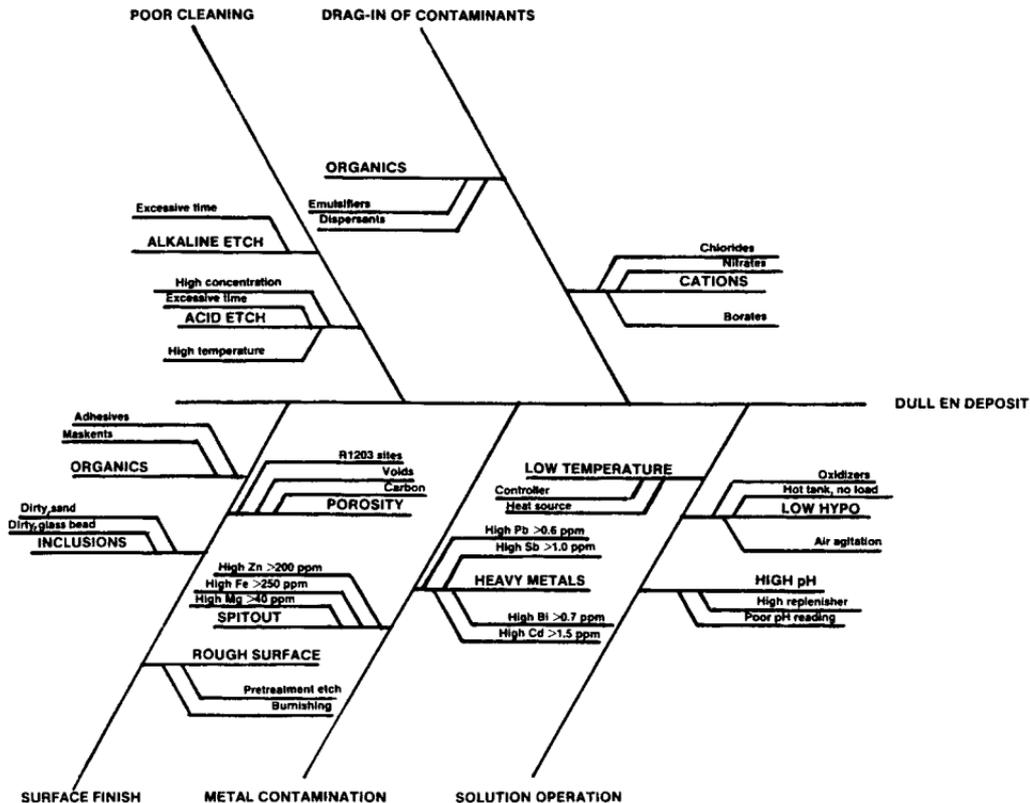


Chart 6.3—Causes of dull electroless nickel deposits. This chart could be used as a starting point to add additional causes that may be unique to the metal finishing facility.

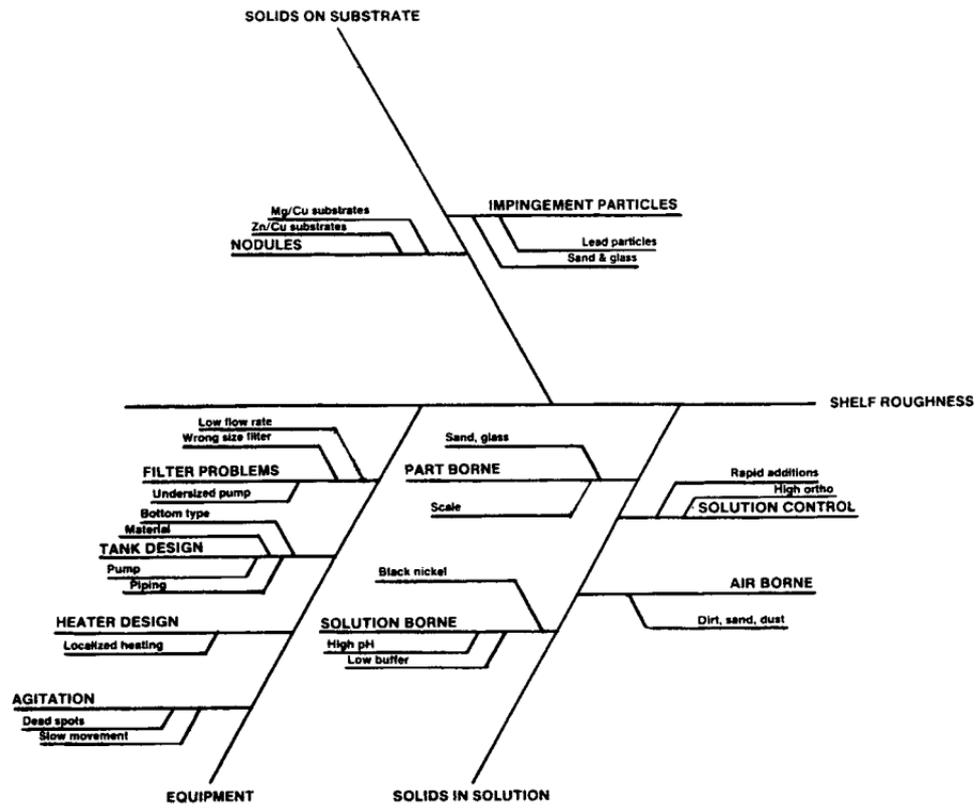


Chart 6.4—Some causes of shelf roughness of electroless nickel deposits. Additional sources of shelf roughness may be present and should be considered in any quality improvement program.

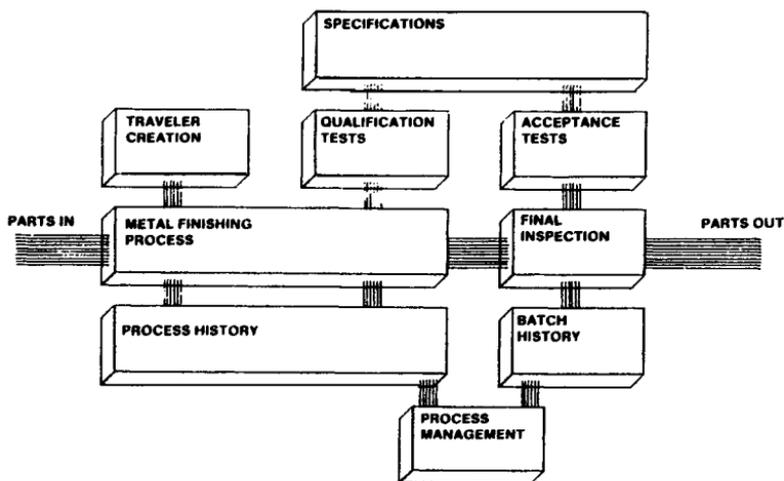


Fig. 6.2—Putting a quality control system together.

Organic contamination within the solution will also cause deposit properties to be compromised. The source of the organic materials may be from the part, facilities and tank, or masking. The problem is manifested by lack of adhesion, porosity, and stress.

Some common sources of organic contamination include maskants, organic materials, oils from within the substrate, plasticizers from hoses and liners, airborne organics, drippage from overhead, and contaminated make-up water. Silicates, though not organic in nature, can adversely contaminate the bath through drag-in from the pretreatment cycle.

Activated carbon treatment of the plating solution at operating temperature can often help reduce or eliminate some types of contaminants. If carbon treatment is used on the solution to remove organic contaminants, care should be taken to replace any desired organic control additives and that the carbon is clean and is not a source of contamination.

Another type of contaminant is *oxidizers*. These materials, such as hydrogen peroxide and nitric acid, will change the deposition potential within the solution and cause black or streaked deposits to be produced. With low levels of volatile oxidizers, heating the solution may help. With higher levels, and with non-volatile oxidizers, the solution must be discarded.

Other conditions that require control are *agitation* and *loading*. These two factors affect the diffusion of nickel ions in the reduction reaction. High agitation and either high or low loading can cause step plating and a low plating rate. Generally, the plating solution will produce coatings when the velocity of the solution is less than 4 ft/sec. This value will be dependent on the solution chemistry and solution operating conditions. At extremely low loads, the

deposition potential may be low enough to prevent the reduction reaction from proceeding. This problem may be observed on sharp edges, such as needles, where the sharp point will not plate. In most cases, this problem can be corrected by selection of solutions that can operate at higher velocities (7 to 10 ft/sec).

### **Testing of Deposit Properties**

The selection of requirements for the electroless nickel deposit are generally made by the purchaser of the coating. These requirements are established in *specifications*. Based on the sampling requirements, a part or specimen must be tested to identify any variation in performance.

The choice of tests that will characterize performance variation specific to the application of the part is important. Two types of tests are employed: acceptance tests and qualification tests. These categories can be used to distinguish tests that will be performed on an individual lot, and those that might be run on a regular basis, such as weekly or monthly.

Acceptance tests include:

- Thickness
- Appearance
- Tolerance
- Adhesion
- Porosity

Qualification tests include:

- Corrosion resistance
- Wear resistance
- Alloy composition
- Internal stress
- Hydrogen embrittlement
- Microhardness

The following list of requirements and test methods have been provided to offer the user of electroless nickel coatings an overview of the options available. The actual organization of requirements and test methods have been published in MIL-C-26074C and ASTM B733 and should be used to maintain a national standard for ordering and performance.

## **TEST METHODS**

### **Appearance**

The coating surface shall have a uniform, metallic appearance without visible defects such as blisters, pits, pimples, and cracks.

Imperfections that arise from surface conditions of the substrate and persist in the coating shall not be cause for rejection. Also, discoloration that results from heat treatment shall not be cause for rejection.

### Thickness Measurement

The thickness shall be measured at any place on the significant surface designated by the purchaser, and the measurement shall be made with an accuracy of better than 5 percent by a method selected by the purchaser. Examples of common measuring devices are shown in Figs. 6.3 and 6.4.

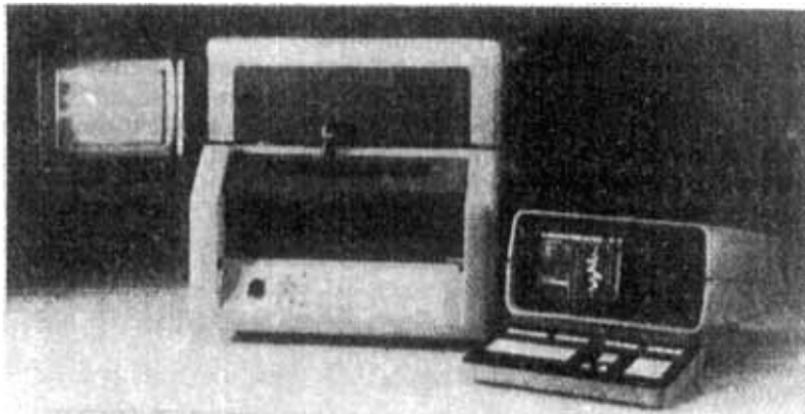


Fig. 6.3—X-ray fluorescence device measures thickness by analyzing the mass per unit area of the electroless nickel deposit according to ASTM B568.

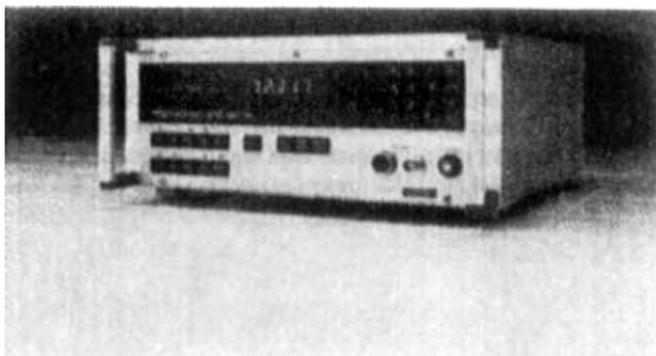


Fig. 6.4—Beta backscatter device also measures thickness by analyzing the mass per unit area of the electroless nickel deposit. There are some limitations to this method, but the cost and availability of instruments makes it an excellent choice for many applications. ASTM B567 can be used to standardize and perform the measurements with this instrument.

**Weigh, Plate, Weigh Method**

Using a similar substrate material, weigh to the nearest milligram before and after plating, ensuring that the part is at the same temperature for each measurement. Calculate the thickness from the increase in weight, surface area, and density of the coating.

*NOTE: The density of the coating will vary with the weight percentage of phosphorus in the coating. For a 9-percent-P alloy, the density is 8 g/cm<sup>3</sup>.*

**Example**—A coupon made of mild steel has a weight of 3198 mg with an area of 19.736 cm<sup>2</sup> before plating. After plating with electroless nickel, the coupon weighs 3583 mg. Calculation for thickness is as follows:

$$T = \frac{3583 \text{ mg (after)} - 3198 \text{ mg (before)}}{8.01 \text{ g/cm}^3 \times 1000 \text{ mg/g}} \div 19.736 \text{ cm}^2$$

$$T = 0.00244 \text{ cm} \times 10,000 \text{ } \mu\text{m/cm}$$

$$T = 24.4 \text{ } \mu\text{m}$$

**Table 6.1**  
**Substrate Densities**  
**For Weigh, Plate, Weigh Method**

Steel, mild 1020	7.86
Stainless steel 316	8.02
Aluminum 2024	2.79
Aluminum 6061	2.70
Copper	8.91

**Metallographic Sectioning**

Plate a specimen of similar composition and metallurgical condition to the article being plated, or use a sample from the lot; mount and polish at 90° to the surface. Using a Vernier Calibrated Microscope, examine the thickness of the deposit and average over 10 readings.

*NOTE: Accurate microscopic metallographic sectioning is very dependent on the sample preparation. Backing springs are recommended to reduce the smearing effects of the polishing step.*

**Micrometer Method**

Measure a part of the test coupon in a specific spot before and after plating, using a suitable micrometer. Ensure that the part is at the same temperature for each measurement and that the surface measured is smooth.

**Beta Backscatter Method**

The coating thickness can be measured by the use of a beta backscatter device. The use of beta backscatter is restricted to base metals that have an atomic number of less than 18 or greater than 40. The actual phosphorus content of the coating shall be taken into consideration; consequently, the measuring device shall be calibrated using specimens of the same substrate having the same phosphorus content as the articles to be tested.

**Magnetic Method**

A magnetic thickness detector is applicable to magnetic substrates plated with autocatalytic nickel deposits that contain more than 10 weight percent phosphorus (non-magnetic) and that have not been heat treated. The instrument must be calibrated with deposits plated in the same bath on steel and whose thickness has been determined by the microscopic method.

**X-ray Spectrometry**

The coating thickness can be measured by X-ray spectrometry. This technique will measure the mass per unit area of the coating applied over the substrate. X-ray spectrometry equipment should be calibrated according to ASTM B568 with standards of known phosphorus and thickness. This method is non-destructive and will produce rapid and accurate results.

**Coulometric Method**

Measure the coating thickness in accordance with ASTM B504. The solution to be used shall be in accordance with manufacturer's recommendations. The surface of the coating shall be cleaned prior to testing.

Standard thickness specimens shall be calibrated with deposits plated in the same solution under the same conditions.

*NOTE: This method is only recommended for deposits in the as-plated condition. The phosphorus content of the coating must be known in order to calculate the thickness of the deposit.*

**Adhesion Measurement****Bend Test**

The sample specimen shall be bent through 180° over a minimum mandrel of 12 mm in diameter or four times the thickness of the specimen and examined at 4X magnification. No detachment of the coating shall occur. Fine cracks in the coating on the tension side of the bend are not an indication of poor adhesion.

**Quench Test**

Heat a plated article for 1 hr in an oven in accordance with Table 6.2 for the appropriate basis metals within  $\pm 10^\circ$  C. Then quench in room temperature water. The appearance of blisters or peeling is evidence of inadequate adhesion.

*NOTE: This test procedure may have an adverse effect on the mechanical properties of the articles tested.*

**Table 6.2**  
**Substrate Heat-Treatment**  
**Temperatures for Quench Test**

Steel	300° C
Zinc	150° C
Copper or copper alloy	250° C
Aluminum or aluminum alloy	250° C

### **Punch Test**

Make several indentations (approximately 5 mm apart) in the coating, using a spring-loaded center punch on which the point has been ground to a 2-mm radius. Blistering or flaking indicates poor adhesion.

### **File Test**

By agreement with the purchaser, a file may be applied to the coated article. A non-significant area shall be filed at an angle of 45° to the coating, so that the base metal/coating interface is exposed. No lifting of the coating shall be observed.

### **Microhardness**

ASTM B578 shall be used for Knoop hardness with a test load of 100 g. The instrument shall be verified on calibrated standard test blocks having a hardness similar to that of the deposit under test.

*NOTE: For thin (less than 25  $\mu\text{m}$ ) deposits using less than 100 g loads, the standard commercial hardness tester produces varied results. This is due to the plastic deformation of the coating and the optical qualities of the instrument.*

On thick (75+  $\mu\text{m}$ ) deposits, a surface microhardness determination using ASTM E384 is permissible.

Conversion of microhardness (Knoop or Vickers) to Rockwell scale is inaccurate and therefore inappropriate (see ASTM E140).

### **Hydrogen Embrittlement**

ASTM F519 shall be used once a month to evaluate the plating process for relief of hydrogen embrittlement. A minimum of three V-notch tensile specimens made of AISI 4340 heat treated to a strength of 260 to 280 ksi shall be plated and loaded at 75 percent or greater of their ultimate notch tensile strength and held for 200 hours. No evidence of fracture or cracks shall exist.

### **Alloy Determination**

There are generally three phosphorus ranges for electroless nickel deposits. Specific types of solution formulations will provide the selection of range of phosphorus in the alloy. Specific confirmation of the alloy can be accomplished by analyzing for nickel and phosphorus by one of the methods described below.

Most applications have been developed using a mid-range of 3 to 9.5 percent phosphorus and are considered typical. Confirmation of the alloy for these coatings can be by nickel or phosphorus, while coatings of less than 3 percent P or greater than 9.5 percent P should use both the nickel and phosphorus analysis to determine the alloy.

### **Preparation of Test Specimens**

There are two general methods of preparing a foil specimen for this test. The most efficient technique is to plate a stainless steel panel with a 25- to 50- $\mu$ m-thick deposit, cut the edges and peel the deposit off the panel.

Another way to produce an autocatalytic nickel phosphorus foil is to deposit a 25- to 50- $\mu$ m-thick coating onto a masked aluminum panel. Then remove the maskant and remove the aluminum by immersing in 10 percent sodium hydroxide solution. When finished, a foil will have been produced that is acceptable for analysis. Although better adhesion is obtained using a zincate treatment, a coherent plate may be obtained by immersing clean aluminum foil in the autocatalytic nickel solution.

### **Determination of Nickel Content—Dimethylglyoxime Method**

Reagents:

- 1:1 v/v concentrated nitric acid (specific gravity 1.42)
- 1 percent solution of dimethylglyoxime

Procedure:

Accurately weigh 0.1 g of autocatalytic nickel deposit and transfer to a 400 mL beaker. Dissolve in 20 mL of 1:1 nitric acid, boil to expel nitrous oxide fumes, then cool and dilute to 150 mL with distilled water. Add approximately 1 g of citric or tartaric acid to complex any ion that may be present and neutralize with ammonium hydroxide to pH 8 to 9.

Heat gently to 60 to 70° C, and while stirring, add 30 mL of dimethylglyoxime reagent. Allow to stand at 60 to 70° C for 1 hr, cool to below 20° C, and filter through a clean sintered glass crucible of No. 4 porosity. Wash the precipitate well with distilled water, dry in an oven at 110° C for 1 hr, cool, and weigh the precipitate as nickel dimethylglyoxime.

$$\% \text{ Ni} = (\text{weight of precipitate} \times 0.2032 \times 100) / \text{sample weight}$$

### Determination of Phosphorus Content

The percentage of phosphorus is determined after dissolution of the deposit in acid, either colorimetrically or volumetrically.

Reagents:

*For dissolution and oxidation*

40 percent v/v concentrated nitric acid (specific gravity 1.42)

2 percent sodium nitrate solution

Approximately 0.1N potassium permanganate solution

*For colorimetric phosphorus analysis*

Molybdate vanadate reagent—Dissolve separately in hot water, 20 g ammonium molybdate and 1 g ammonium vanadate, then mix the two solutions. Add 200 mL of concentrated nitric acid (specific gravity 1.42) and dilute to 1 L.

*For volumetric phosphorus analysis*

**Solution A:** Dissolve 15 g of ammonium molybdate in 80 mL distilled water. Add 6 mL ammonium solution (specific gravity 0.880) and dilute to 100 mL.

**Solution B:** Dissolve 24 g ammonium nitrate in 60 mL distilled water. Add 33 mL concentrated nitric acid and dilute to 100 mL.

Procedure for dissolution and oxidation:

1. Dissolve 0.19 to 0.21 g (weigh accurately) of autocatalytic nickel deposit in 50 mL of 40 percent v/v nitric acid solution.
2. Heat gently until the deposit is fully dissolved. Then boil to remove brown fumes.
3. Dilute to approximately 100 mL, bring to the boil, and add 20 mL of approximately 0.1N potassium permanganate solution.
4. Boil for 5 minutes.
5. Add 2 percent solution of sodium nitrite dropwise until the precipitated manganese dioxide is dissolved.
6. Boil for 5 minutes, then cool to room temperature.
7. Dilute the solution in a volumetric flask to 250 mL and mix well.

At this stage, the phosphorus content may be estimated either colorimetrically or volumetrically, as described below.

Procedure for colorimetric analysis:

1. Transfer 10 mL of the solution from step 7 above to a 100-mL standard flask, add 50 mL distilled water, 25 mL molybdate-vanadate reagent, dilute to the mark with water, and mix well.
2. Read the absorption at 420 nm after 5 minutes, using 1 cm glass cells with water in the reference cell. Read off the concentration from a previously prepared calibration curve.

$\% P = \text{mg P from graph/weight of sample (mg)}$

Procedure for preparation of calibration curve:

1. Dry potassium dihydrogen orthophosphate at 115° C for 1 hour.
2. Weigh out 0.4392 g, dissolve in water, and make up to 1 L of solution (1 mL = 0.1 mg phosphorus).
3. Prepare a calibration curve by adding 25 mL of reagent to 2 mL, 4 mL, 6 mL, 8 mL, and 10 mL liquids of this standard solution in 100 mL standard flasks and diluting to the mark. Read the absorption of these solutions exactly as for the estimated reading at 420 nm, as described above. Plot a calibration curve of absorption against mg phosphorus in samples of 0.2 mg, 0.4 mg, etc., up to 1.0 mg when prepared as above.

Procedure for volumetric analysis:

1. Transfer 10 mL of the solution from step 7 above to a stoppered flask and dilute to 100 mL with distilled water.
2. Warm to 40 to 50° C (**do not exceed this temperature**) and slowly add 50 mL of ammonium molybdate reagent while stirring.
3. Stopper the flask.
4. Agitate the flask vigorously for 10 minutes.
5. Allow the flask to stand for 30 minutes and filter through a Whatman No. 542 filter paper.
6. Wash the flask and precipitate with 1 percent potassium nitrate until the filtrate will not decolorize 1 mL of water containing 1 drop of 0.1N sodium hydroxide and 1 drop of phenolphthalein. This will require about 100 mL of the washing liquid.
7. Place the paper and precipitate in the original flask, add 50 mL water, and shake well.
8. Add 10 mL of 0.1N sodium hydroxide solution and shake well to dissolve the precipitate.
9. Add phenolphthalein indicator and back-titrate with 0.1N hydrochloric acid. Let "X" mL be the titration.

$\% P = [25 \times (10-X) \times 0.01349]/\text{weight of sample}$

### Spectra Analysis

A suitable method using emission spectra produced by Inductively Coupled Plasma (ICP) would be acceptable for analysis in nickel, phosphorus, and trace elements.

The following lines have been found to have low interferences when using argon ICP techniques. AA standards should be used for this analysis. Phosphorus standards should be made weekly to ensure accuracy.

Ni 216.10 nm	Al 202.55 nm	Cr 284.32 nm	Pb 283.30 nm
P 215.40 nm	Cd 214.44 nm	Cu 324.75 nm	Sn 189.94 nm
P 213.62 nm	Co 238.34 nm	Fe 238.20 nm	Zn 206.20 nm

## Porosity Measurement

The test to be applied shall be decided by the purchaser in agreement with the plater.

### Porosity Tests for Ferrous Substrates

#### Ferroxyl Test

The test solution is prepared by dissolving 25 g of potassium ferrocyanide and 15 g of sodium chloride in 1 L solution. The part is cleaned and immersed for 5 sec in the test solution at 25° C, followed by water rinsing and air drying. Blue spots visible to the unaided eye will form at pore sites. Their allowable number should be specified.

Alternately, strips of suitable paper (e.g., "wet strength" filter paper) are first immersed in a warm (about 35° C) solution containing 50 g/L of sodium chloride and 50 g/L of white gelatin and then allowed to dry. Just before use, they are immersed in a solution containing 50 g/L sodium chloride and 1 g/L of a non-ionic wetting agent, and pressed firmly to make satisfactory contrast onto the cleaned nickel surface to be tested and allowed to remain for 30 minutes.

If papers should become dry during the test, they should be moistened again, in place, with the sodium chloride solution. The papers are then removed and introduced at once into a solution containing 10 g/L potassium ferrocyanide to produce sharply defined blue markings on the papers, wherever the basis metal was exposed by discontinuities in the coating, leading to attack by the sodium chloride and transference of the ion components to the paper. If necessary, the same area may be retested.

#### Hot Water Test

Immerse the part to be tested in a beaker filled with aerated water at room temperature. Apply heat to the beaker at such a rate that the water begins to boil in not less than 15 minutes, and not more than 20 minutes. Then remove the part from the water and air dry. Examine the part for rust spots, which will indicate pores.

Aerated water is prepared by bubbling clean compressed air through a reservoir of distilled water by means of a glass diffusion disc for at least 24 hours. The pH of the aerated water should be  $6.7 \pm 0.5$ . The test parts should be covered by at least  $30 \pm 5$  mm of aerated water.

#### Neutral Salt Spray

Testing in accordance with ASTM B117 shall be conducted monthly on the plating process. Coat a 4 x 6 x 0.20 AISI 4130 steel panel with 0.0015 in. of deposit. Wash edges and expose in salt spray chamber for a minimum of 240 hours. This panel shall have a rating of 9.5 or better in accordance with ASTM B537.

*NOTE: This test can be made more aggressive by reducing the plating thickness and increasing the exposure time (e.g., 0.0005 in. for 1000 hours).*

page 186

#### Hot Chloride Porosity Test

Immerse a steel part in 50 percent reagent HCl for 3 hours at 83° C. After testing, the acid shall not be significantly discolored or the part will have exfoliation or

blisters. Equipment needed to perform this test: a glass beaker, hot plate, thermometer, and a timer.

The purpose of this test is to locate pore sites in the coating when the pore cell potential is greater than 150 mV. Rapid corrosion will occur, causing significant failure of the coating and substrate. A polyethylene cover affixed to the beaker with a large rubber band can be used to reduce the vapor and evaporation of the acid. This test should be performed under a fume hood to remove acid vapor.

### **Porosity Test for Aluminum Substrates**

Wipe the specimens with a 10 percent solution of sodium hydroxide. After 3 min, rinse and apply a solution of sodium alizarin sulfonate (9,10-anthraquinon-1,2-dihydroxy-3-sulfonate, sodium salt) to the specimen. This solution is prepared by dissolving 1.5 g methyl cellulose in 90 mL boiling water to which, after cooling, a solution of 0.1 g sodium alizarin sulfonate dissolved in 5 mL ethanol is added.

After 4 min, apply glacial acetic acid at ambient temperature until the violet color disappears. Any red spots remaining indicate pores.

### **Porosity Test for Copper Substrates**

Wipe the specimen with glacial acetic acid at ambient temperature. After 3 min, apply to the specimen surface a solution of potassium ferricyanide, prepared by dissolving 1 g of potassium ferricyanide and 1.5 g of methyl cellulose in 90 mL of boiling deionized water. After 2 to 3 min, the appearance of brown spots will indicate pores.

## **Standard Method for Measuring Corrosion Rate**

### **Scope**

This method establishes the apparatus, specimen preparation, test procedure, evaluation, and reporting of the corrosion rate of autocatalytic nickel deposits. The results are determined by using linear polarization and potentiodynamic techniques, and can be used to rank the coatings in order of corrosion resistance.

This test method is applicable to electroless nickel deposits applied to specimens of G5 specification and corroded in an artificial environment.

This test method is provided for use in an interlaboratory corrosion procedure for evaluating electroless nickel deposits.

### **Applicable Documents**

ASTM standards:

G3 Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing

G5 Standard Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements

G15 Definition of Terms Relating to Corrosion and Corrosion Testing

G59 Practice for Conducting Potentiodynamic Polarization Resistance Measurements

### Summary of Method

The specimen (working electrode) is prepared by plating in an electroless nickel solution a steel G5 plug. The plug is then cleaned and mounted in an electrochemical cell of G5 design. The cell is charged with a test solution at ambient temperature and purged with nitrogen. The cell is then pressurized with the gas in question and heated to the desired temperature. Measurements are then taken after 1000 sec to find the corrosion potential ( $E_{corr}$ ). Polarization measurements are then made to determine the instantaneous corrosion rate for the applied pressure and temperature. The curves from various conditions and alloys can then be compared and the relative corrosion resistance can be established.

### Significance and Use

The significance of these tests is that they can be used to rank electroless nickel deposits in order of their corrosion resistance. These tests can then be used to develop a comprehensive corrosion monitoring program to evaluate the substrate pretreatment and electroless nickel deposit.

Results from these tests produce quantitative values as to the corrosive nature of the environments and the protection afforded by specific electroless nickel deposits under laboratory conditions.

### Apparatus

The following required equipment is described in ASTM G5:

1. Potentiostat calibrated according to ASTM G5
2. Potential measuring device
3. Current measuring device
4. Saturated calomel electrode
5. Salt bridge probe

The specimen (working electrode) to be tested is plated with electroless nickel and post-treated with the desired process. The specimen can be made from any material to the following physical dimensions: 1/2 in. (12.7 mm) long, 3.8 in. (9.5 mm) diameter, with a 3-84 tapped hole at one end. The entire surface shall be 16 rms or better.

*NOTE: The specimens used in this ASTM program are made from C1215 steel.*

The polarization cell shall be made to the following ASTM G5 specifications:

1. Carbon or platinum counter electrodes shall be used in the cell.
2. The salt bridge shall be adjustable and able to be located near the tip of the working electrode.
3. The electrolytes shall be agitated constantly with a magnetic stirrer.
4. The cell shall be purged constantly with  $N_2$  gas.
5. The cell shall be able to operate at 1 atmosphere.
6. The cell shall be able to operate at a temperature of 22° C.
7. The specimen holder shall be designed and maintained to form a tight connection between the specimen and the teflon gasket of the holder.

## Reagents

Corroding Electrolyte I is prepared by dissolving 12.5 g of reagent grade sodium chloride (NaCl) into 900 mL of Type I reagent water.\* Adjust pH to  $7.8 \pm 0.1$  with sodium hydroxide. Fill to 1000 mL with Type I reagent water.

Corroding Electrolyte II is prepared by dissolving 40 g of reagent grade sodium chloride (NaCl) into 1000 mL of Type I reagent water.

## Specimen Preparation

Prepare the specimen by the following steps:

1. Vapor degrease or solvent wash.
2. Caustic clean with appropriate cleaner for steel or aluminum substrate.

Note mounting hole will expose substrate alloy to cleaning solution.

3. Rinse with Type I reagent water.
4. Wash with 25 percent sulfuric acid for 60 sec at 25° C.
5. Rinse with Type I reagent water.
6. Mount the specimen on the electrode holder. Care should be exercised not to contaminate or disturb the cleaned surface.

## Test Parameters

Potentiodynamic polarization:

1. Initial potential -100 mV from  $E_{corr}$
2. Final potential -600 mV
3. Vertex potential +1000 mV
4. Input anodic tafel constant (ATC) 0.145; cathodic tafel constant (CTC) 0.150
5. Scan rate 2.0 mV/sec

Linear polarization:

1. Initial potential -30 mV  $E_{corr}$
2. Final potential 30 mV  $E_{corr}$
3. Anodic and cathodic tafel constant from potentiodynamic
4. Scan rate 0.2 mV/sec

Specimen physical parameters:

1. Area 4.285 cm<sup>2</sup>
2. Density 7.95 g/cm<sup>3</sup>
3. Equivalent weight 28.51 mols/electron

## Wear Analysis

### Abrasion Resistance

Abrasion resistance can be measured by a Taber Abrader using a CS-10 wheel. Wear specimens should be dressed for the first 1000 cycles and then weighed. The CS-10 wheels should be redressed for 50 cycles for each 1000 cycles of wear on the specimen. Typical tests are taken to 10,000 cycles with a range of 15 to 30

\*Type I reagent water is defined in ASTM D1193 as 16.67 M ohm-cm resistivity.

mg/1000 cycles for as-plated deposits, and 6 to 18 mg/1000 cycles for precipitation-hardened deposits. The test is not precise, but can be used to characterize the differences between coatings when several specimens are tested.

### **Adhesive Wear Resistance**

Adhesive wear resistance can be tested by several means. These include pin on disc, block on ring, and pin on notch. Each of these types of adhesive wear tests simulate slight differences in metal-to-metal wear. To evaluate the specific wear for a particular application, the correct wear test method must be selected. Conditions such as temperature, lubrication, load, vibration, wear scar, velocity, and others will affect the results requiring careful study of the test methods before a test can be selected.

The Alpha-LFW1 is a block-on-ring test that has been found to provide wear information on electroless nickel coatings. The Falex tester is a pin-on-notch device that provides information on high load wear. Both of these tests can be run dry or lubricated, and can be used to characterize the differences between coatings.

### **Stress Analysis**

The intrinsic stress of the deposit can be determined using ASTM B636. This test uses a spiral contractometer, plating the spiral and measuring the amount of movement in the helix while the spiral is plating. The amount of intrinsic stress in the deposit is determined by the rate of swing in a needle attached to the spiral. The movement is magnified by a factor of 10, with readings being taken while the process is operating. After the measurement of intrinsic stress has been taken at plating temperature, the helix can be removed and cooled. A second reading can be taken, providing the total stress, and then the thermal component can be calculated:

$$\text{Spiral total stress} = \text{intrinsic stress} + \text{thermal stress}$$

The results can be used to predict when adhesion may be compromised on aluminum and other alloys, as well as the preference for certain types of corrosion.

Other methods of analysis for total stress have been developed using a rigid strip. Strips are first plated on both sides, then one side is removed with a stripper. The thickness of the strip and the coating are measured, and then the amount of bow in the strip is measured. Calculations can be made from this information, and the total stress in the part can be selected.

## **POST-TREATMENTS**

The quality control of an electroless nickel deposit implies that certain post-treatments have been completed. These are generally used to improve the

deposit adhesion or increase the hardness of the deposit by precipitation of phosphorus to nickel phosphide.

In most specifications, the requirements for heat treatment are described. Generally there are no tests for these processes, and self-certification must be used. In some cases, a test may exist that is destructive, and therefore not usable.

MIL-C-26074C and ASTM B733 both use the same classification system to describe the post-heat treatment of the deposit. These documents use the term *class* and establish the steps to reduce the potential for hydrogen embrittlement, increase the adhesion of the coating, improve the fatigue properties of the part(s), and increase the wear resistance and hardness of the coating.

## **Classes of Electroless Nickel Coatings**

### **Class 1**

As plated, no treatment other than hydrogen embrittlement relief at  $190 \pm 10^\circ \text{C}$  for steels with a tensile strength of 1051 MPa or greater.

### **Class 2**

Heat treated for hardness, the coating shall be heat treated to a minimum hardness of 850 Knoop (100 g load). This hardness can be produced by heat treating the coating at  $400^\circ \text{C}$  for 60 minutes. Higher temperatures for shorter times may be used.

### **Class 3**

Heat treatment at 180 to  $200^\circ \text{C}$  for 2 to 4 hours to improve coating adhesion on aluminum.

### **Class 4**

Heat treatment at 120 to  $130^\circ \text{C}$  for a minimum of 1 hour to improve adhesion on heat-treatable (age-hardened) aluminum alloys and carburized steels.

### **Class 5**

Heat treatment at 140 to  $150^\circ \text{C}$  for a minimum of 1 hour to improve adhesion on non-age-hardened aluminum and beryllium alloys.

The use of the shop traveler to record the completion of the heat treatment, as well as a notation on the chart record of the oven, is a standard practice.

Additional post-treatments such as silicates, water glasses, waxes, and chromates, are sometimes applied to prevent staining and oxidation of the nickel. The analysis of these treatments are complicated and seldom tested. Contact resistance tests are generally used if the treatment requires testing.

## **QUALITY CONTROL**

To conclude, the electroless nickel facility must have a quality control system. The platers need to identify how the parts are to be processed. In addition, they

must maintain the chemistry, qualify the processes, and complete the acceptance tests as required by the specifications.

The system can be operated from a single notebook or from a multiuser computer system. The quality control program can be highly complex, or just cover the essentials.

In the end, it is dedicated people who must build and follow the quality control system. It is people who will produce higher levels of quality and make it possible to extend the performance of electroless nickel deposits into new markets and applications.